Transition Metal Complexes with Sulfur Ligands, 123[◇]

Synthesis and Reactivity of New Complexes Containing the [Ru("S_4")] Fragment ["S_4"$^{2-}$ = 1,2-Bis(2-mercaptophenylthio)ethane(2−)]

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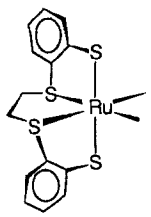
In order to synthesize labile and well-soluble [Ru(L)(L')("S_4")] complexes, [Ru(Cl)$_2$(DMSO)$_4$] was treated with "S_4"-Na_2 ["S_4"$^{2-}$ = 1,2-bis(2-mercaptophenylthio)-ethane(2−)] yielding [Ru(DMSO)$_2$("S_4")] (**1**) which contains two labile DMSO ligands. An X-ray structural analysis of **1** verifies that both DMSO ligands are coordinated via their S atoms. The reaction of **1** with small ligands such as PR_3 (R = Et, *n*Pr, *n*Bu) or tetrahydrothiophene (THT) leads to substitution of both DMSO ligands yielding [Ru(PR_3)$_2$("S_4")] (R = Et **3a**, *n*Pr **3b**, *n*Bu **3c**) and [Ru(THT)$_2$("S_4")] **2**, respectively, while bulky phosphane ligands such as PCy_3 and P*i*Pr$_3$ substitute one DMSO ligand to yield [Ru(DMSO)(PR_3)("S_4")] (R = *i*Pr **4a**, Cy **4b**). X-ray structural analyses of [Ru(P*n*Pr$_3$)$_2$("S_4")] · 0.5 MeOH (**3b** · 0.5 MeOH), [Ru(P*n*-Bu$_3$)$_2$("S_4")] (**3c**), and [Ru(PMe_3)$_2$("S_4")] (**3d**) confirm the pseudo-octahedral coordination of the Ru centers by four S-donors and two *cis* P-donors and reveal close similarities between the three complexes. Comparison of the structural parameters of **3b** · 0.5 MeOH, **3c** and **3d** with those of [Ru(PPh$_3$)$_2$("MeS_4")] ["MeS_4"$^{2-}$ = 1,2-bis(2-mercaptophenylthio)propane(2−)] indicates that the inertness towards substitution of **3b** · 0.5 MeOH, **3c** and **3d** as opposed to the substitution lability of [Ru(PPh$_3$)$_2$("MeS_4")] is caused by the small cone angles of the alkyl phosphanes. In the DMSO/PCy_3 complex **4b** both coligands are labile, and which one is substituted depends on the size of the entering ligand. The reactions of **4b** with P*n*R$_3$ yield [Ru(DMSO)(PR_3)("S_4")] (R = *n*Pr **4c**, *n*Bu **4d**) in contrast to the reaction with CO, PMe_3, and SMe_2 which give [Ru(CO)(PCy_3)("S_4")] (**5b**), [Ru(P-Me_3)(PCy_3)("S_4")] (**6**), and [Ru(SMe_2)(PCy_3)("S_4")] (**7**), respectively. In an analogous manner, the CO complexes [Ru-(CO)(PR_3)("S_4")] (R = *i*Pr **5a**, *n*Bu **5c**) have been obtained by treatment of **4a** and **4d** with CO. The reactions of **4a** and **4b** with S_8 yielded the readily soluble μ-S_2 complexes [μ-S_2\{Ru(PR_3)("S_4")\}$_2$] (R = *i*Pr **8a**, Cy **8b**). The spectroscopic data of complex **8b** and its cyclic voltammogram, which exhibits four quasi-reversible redox waves, indicate a strong electronic coupling of the two [Ru(PCy_3)("S_4")] fragments via the μ-S_2 bridge.

Introduction

The activation and stabilization of small molecules such as CO, N_2, H_2, or N_2H_2 by transition metal-sulfur complexes is of interest with regard to industrial catalyses and enzymatic processes such as, for example, hydrotreatment processes[1], N_2 fixation[2], biological H_2 production[3], or CO reduction[4].



The complex fragment [Ru("S_4")] is able to coordinate a large variety of molecules as coligands resulting in [Ru(L)(L')("S_4")] complexes. The coligands L and L' can be identical or different such as in [Ru(CO)$_2$("S_4")], [Ru(PMe_3)$_2$("S_4")], [Ru(PPh_3)$_2$("S_4")][5a], or [Ru(L')(PPh_3)-("S_4")][5a–c] in which L' = CO, N_2H_2, N_2H_4, HCl, etc. [Ru(PMe_3)$_2$("S_4")] and [Ru(PPh_3)$_2$("S_4")] represent two extremes of reactivity. While [Ru(PMe_3)$_2$("S_4")] is practically inert towards substitution, [Ru(PPh_3)$_2$("S_4")] readily exchanges one PPh_3 ligand under ambient conditions and proved to be a suitable precursor for the synthesis of [Ru(L')(PPh_3)("S_4")] complexes. However, to date [Ru(PPh_3)$_2$("S_4")] is the only known labile bis(phosphane) complex of the type [Ru(PR_3)$_2$("S_4")] and the remaining PPh_3 ligand in the resultant [Ru(L')(PPh_3)("S_4")] species is found to be inert towards further substitution. Thus, it was impossible to study the influence of other coligands, e.g., other phosphanes, upon the activation or stabilization of the L' ligands. In addition, all attempts to obtain [Ru(L')(PPh_3)("S_4")] complexes with L = N_2, H_2 or H^-,

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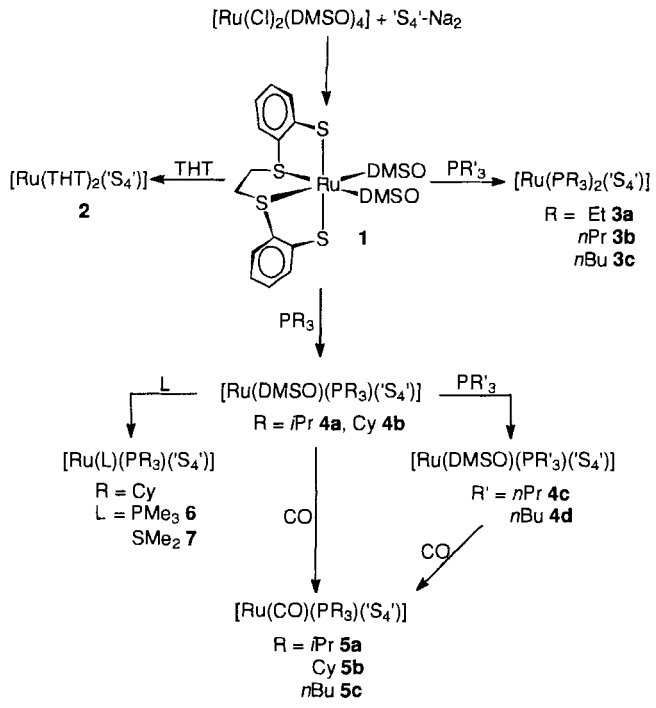
these being of particular interest in relation to non-enzymatic dinitrogen fixation and dihydrogen activation, remained unsuccessful. Finally, the majority of [Ru(L')(PPh$_3$)("S$_4$")] complexes exhibit relatively low solubility in all common solvents. These shortcomings of the [Ru(PPh$_3$)("S$_4$")] system prompted us to search for [Ru("S$_4$")] complexes which are more labile and show improved solubility. We particularly focussed on alkylphosphane [Ru(PR$_3$)("S$_4$")] species, because we recently found that the related [μ-N$_2$H$_2${Fe(PR$_3$)("S$_4$")}$_2$] complexes are accessible in unprecedented high yields, albeit only when the phosphane ligands are P*n*Pr$_3$ or P*n*Bu$_3$. In contrast, analogous PMe$_3$ or PPh$_3$ derivatives could not be obtained[6].

Results

In an effort to obtain substitution labile [Ru(L)(L')("S$_4$")] complexes, we first synthesized [Ru(DMSO)$_2$("S$_4$")] (**1**). Complex **1** was obtained as a yellow-brown solid when [Ru(Cl)$_2$(DMSO)$_4$] was treated with "S$_4$"-Na$_2$ in methanol (Scheme 1). Complex **1** is highly reactive. A suspension of **1** in methanol readily decomposed at temperatures above 40 °C, to give an insoluble brown solid, the IR spectrum (KBr discs) of which was consistent with the formation of polynuclear [Ru("S$_4$")]$_x$.

Scheme 1. Reactions of [Ru(DMSO)$_2$("S$_4$")] (**1**) and its derivatives



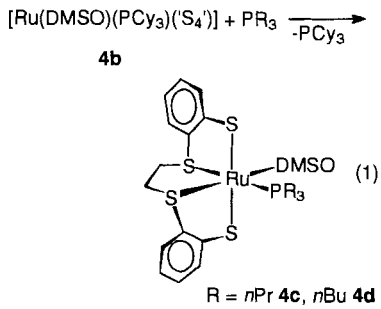
The reactive DMSO complex **1** proved to be a versatile starting material for the synthesis of other [Ru(L)(L')("S$_4$")] complexes. In the course of these investigations, it proved unnecessary to isolate **1** since the syntheses could be carried out as "one pot" reactions in methanol.

Under ambient conditions, a controlled substitution of the DMSO ligands of complex **1** proved feasible with sulfur donor ligands such as tetrahydrothiophene (THT) and with phosphanes. Treatment of **1** with THT yielded [Ru(THT)$_2$("S$_4$")] (**2**), in which the Ru center is surrounded exclusively by sulfur donors. Sterically less demanding phosphanes such as PEt$_3$, P*n*Pr$_3$, and P*n*Bu$_3$ gave the corresponding bis(phosphane) complexes [Ru(PEt$_3$)$_2$("S$_4$")] (**3a**), [Ru(P*n*Pr$_3$)$_2$("S$_4$")] (**3b**) and [Ru(P*n*Bu$_3$)$_2$("S$_4$")] (**3c**). In contrast, the use of sterically more demanding or very bulky phosphanes such as P*i*Pr$_3$ or PCy$_3$ led to the substitution of only one DMSO ligand and the formation of the monophosphane derivatives [Ru(DMSO)(P*i*Pr$_3$)("S$_4$")] (**4a**) and [Ru(DMSO)(PCy$_3$)("S$_4$")] (**4b**).

Attempts to substitute only one DMSO ligand in **1** by P*n*Pr$_3$ or P*n*Bu$_3$ did not meet with any success. Treatment of **1** with one equivalent of these phosphanes yielded only 1:1 mixtures of the bis(phosphane) complexes **3b** and **3c** and the starting complex **1**.

The bis(phosphane) complexes **3a**–**3c** proved to be practically as inert towards substitution as the previously described [Ru(PMe$_3$)$_2$("S$_4$")] complex, and thus no [Ru(L)(PR$_3$("S$_4$")] derivatives (PR$_3$ = PEt$_3$, P*n*Pr$_3$, P*n*Bu$_3$, L = N$_2$H$_4$, CO) could be obtained.

[Ru(DMSO)(PCy$_3$)("S$_4$")] (**4b**) is a versatile precursor complex. Both the PCy$_3$ and the DMSO ligand of **4b** are labile, and which one of them is substituted appears to be critically dependent on the size of the entering ligand. Upon treatment of **4b** with P*n*Pr$_3$ and P*n*Bu$_3$, the PCy$_3$ ligand was substituted according to eq. (1).



This reaction allowed the isolation of the phosphane/DMSO complexes [Ru(DMSO)(P*n*Pr$_3$)("S$_4$")] (**4c**) and [Ru(DMSO)(P*n*Bu$_3$)("S$_4$")] (**4d**), which had not been accessible in the "one pot" reactions of [Ru(DMSO)$_2$("S$_4$")] (**1**) with P*n*Pr$_3$ or P*n*Bu$_3$.

In contrast, when [Ru(DMSO)(PCy$_3$)("S$_4$")] (**4b**) was treated with small molecules such as CO, PMe$_3$, or SMe$_2$, it was the DMSO ligand, and not the PCy$_3$ ligand, which was exchanged. These exchange reactions yielded [Ru(CO)(PCy$_3$)("S$_4$")] (**5b**), [Ru(PMe$_3$)(PCy$_3$)("S$_4$")] (**6**), and [Ru(SMe$_2$)(PCy$_3$)("S$_4$")] (**7**). Similarly, the phosphane/DMSO complexes **4a** and **4d** underwent CO for DMSO exchange, yielding [Ru(CO)(P*i*Pr$_3$)("S$_4$")] (**5a**) and [Ru(CO)(P*n*Bu$_3$)("S$_4$")] (**5c**), respectively. The phosphane ligands in [Ru(DMSO)(PR$_3$)("S$_4$")] influence the reaction conditions of the DMSO/CO exchange. The P*i*Pr$_3$ and PCy$_3$ complexes **4a** and **4b** readily exchanged their DMSO ligands for CO at standard pressure, but the P*n*Bu$_3$ complex **4d** required elevated CO pressure (30 bar).

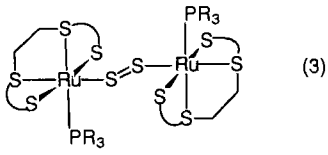
The lability of the PR_3 ligands in $[Ru(PMe_3)(P-Cy_3)(\text{"}S_4\text{"})]$ (**6**) was probed with CO. According to eq. (2), previously reported $[Ru(PMe_3)(CO)(\text{"}S_4\text{"})]$[5a] was formed, indicating that in **6** the PCy_3 ligand is more labile than PMe_3.

$$[Ru(PMe_3)(PCy_3)('S_4')] + CO \longrightarrow \underset{\mathbf{6}}{} [Ru(PMe_3)(CO)('S_4')] + PCy_3 \quad (2)$$

The DMSO complexes **4a** and **4b** proved to be precursors for very soluble S_2 bridged complexes[7,8]. Treatment with elemental sulfur yielded the dark-blue complexes $[\mu\text{-}S_2\{Ru(P\mathit{i}Pr_3)(\text{"}S_4\text{"})\}_2]$ (**8a**) and $[\mu\text{-}S_2\{Ru(PCy_3)(\text{"}S_4\text{"})\}_2]$ (**8b**), according to eq. (3).

$$2\,[Ru(DMSO)(PR_3)('S_4')] + S_{8(exc)} \longrightarrow$$

R = *i*Pr **4a**, Cy **4b**



(3)

R = *i*Pr **8a**, Cy **8b** (= C_6H_4

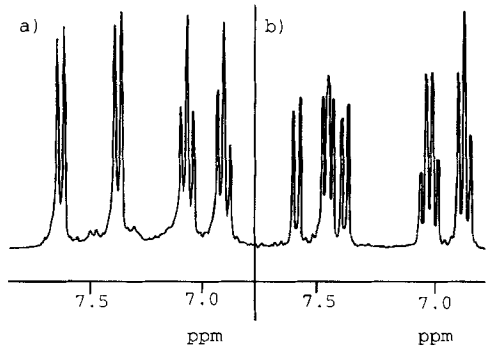
General Properties and Characterization of the Complexes

All complexes described above are readily soluble in CH_2Cl_2, $CHCl_3$, and THF, but are practically insoluble in CH_3OH, Et_2O, and *n*-hexane. They have been characterized by the usual spectroscopic methods.

The IR spectra of the complexes (KBr discs) exhibit the typical absorption patterns of the $[M(\text{"}S_4\text{"})]$ fragments. The DMSO/phosphane complexes show strong absorptions in the region of 1090–1080 cm^{-1}, indicating DMSO coordination via the S atom[9]. The bis(DMSO) complex **1** exhibits an additional ν(SO) band at 1020 cm^{-1}. $[Ru(PMe_3)(P-Cy_3)(\text{"}S_4\text{"})]$ (**6**) displays a characteristic δ(PCH) band (954 cm^{-1}) for the PMe_3 ligand, while the CO complexes **5a–c** show characteristic ν(CO) bands in the region of 1955 cm^{-1}.

The NMR spectra allow a clear distinction to be made between C_2 and C_1 symmetric complexes. For example, in the ^{1}H-NMR spectra the splitting pattern of the aromatic "S_4" protons in C_2 symmetric complexes such as $[Ru(DMSO)_2(\text{"}S_4\text{"})]$ (**1**) changes in a characteristic way when the symmetry is lowered to C_1 such as in $[Ru(DMSO)(PCy_3)(\text{"}S_4\text{"})]$ (**4b**) (Figure 1). In addition, C_2 symmetric complexes give rise to six signals, while C_1 symmetric complexes show 12 signals for the aromatic carbon atoms of the "S_4" ligand in the $^{13}C\{^1H\}$ NMR spectra.

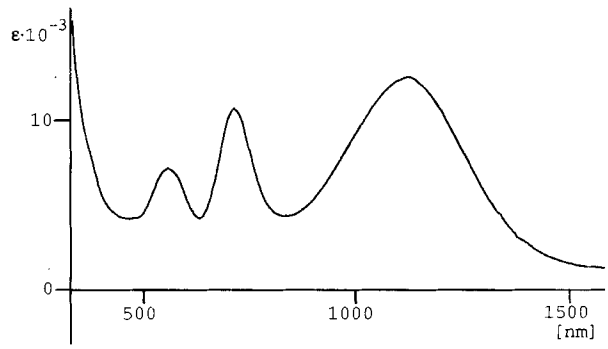
Figure 1. Splitting patterns of the aromatic protons in the ^{1}H-NMR spectra of a) $[Ru(DMSO)_2(\text{"}S_4\text{"})]$ (**1**) in CD_2Cl_2 and b) $[Ru(DMSO)(PCy_3)(\text{"}S_4\text{"})]$ (**4b**) in CD_2Cl_2



A further notable feature of the ^{1}H-NMR spectra of the DMSO complexes is that the chemical shifts of the two CH_3 singlets are consistent with a DMSO coordination via the S atoms[9].

In contrast to the yellow mononuclear complexes, the binuclear $\mu\text{-}S_2$ complexes **8a** and **8b** are dark-blue. Their electronic spectra exhibit three characteristic and intense absorption bands in the Vis/NIR region (Figure 2). As discussed previously, these bands can be assigned to π-π* transitions in a 4c-6e π-system that extends over the Ru–S–S–Ru unit[8].

Figure 2. UV/Vis/NIR spectrum of $[\mu\text{-}S_2\{Ru(PCy_3)(\text{"}S_4\text{"})\}_2]$ (**8b**) in CH_2Cl_2



X-Ray Structure Analysis of $[Ru(DMSO)_2(\text{"}S_4\text{"})]$ (1) and $[Ru(PR_3)_2(\text{"}S_4\text{"})]$ [R = Me (3d), *n*Pr (3b), *n*Bu (3c)]

The molecular structures of $[Ru(DMSO)_2(\text{"}S_4\text{"})]$ (**1**), $[Ru(P\mathit{n}Pr_3)_2(\text{"}S_4\text{"})]$ (**3b**), $[Ru(P\mathit{n}Bu_3)_2(\text{"}S_4\text{"})]$ (**3c**), and $[Ru(PMe_3)_2(\text{"}S_4\text{"})]$ (**3d**) were determined by X-ray structure analyses. Figure 3 shows the molecular structures of **1**, **3b** ·

0.5 MeOH, **3c** and **3d**. Selected distances and angles are summarized in Table 1.

Figure 3. ORTEP plots of a) **1**, b) **3b** · 0.5 MeOH, c) **3c**, and d) **3d** drawn with 50% probability ellipsoids (H atoms and solvent molecules are omitted)

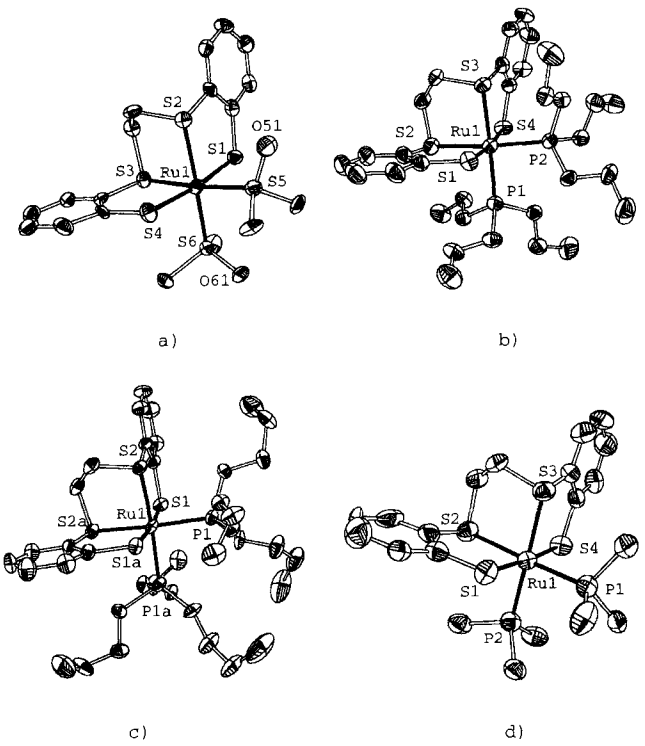


Table 1. Selected distances [pm] and angles [°] of [Ru(DMSO)$_2$("S$_4$")] (**1**), [Ru(P*n*Pr$_3$)$_2$("S$_4$")] · 0.5 MeOH (**3b** · 0.5 MeOH), [Ru(P*n*Bu$_3$)$_2$("S$_4$")] (**3c**), and [Ru(PMe$_3$)$_2$("S$_4$")] (**3d**)

	1	**3b**·0.5 MeOH	**3d**	**3c**
Ru–S1	240.3(3)	239.5(4)	239.1(4)	S1a 239.8(2)
Ru–S2	235.0(3)	235.8(4)	239.1(4)	S2a 236.8(2)
Ru–S3	234.6(3)	236.8(4)	239.3(4)	S2 236.8(2)
Ru–S4	240.3(3)	239.8(4)	239.4(4)	S1 239.8(2)
Ru–P1	S5 229.5(3)	233.3(4)	228.7(4)	P1a 232.3(2)
Ru–P2	S6 230.1(3)	233.4(4)	229.3(4)	P1 232.3(2)
S1–Ru–S4	173.50(10)	172.8(1)	176.4(1)	172.8(1)
S2–Ru–S3	87.51(9)	87.3(1)	85.1(1)	86.6(1)
P2–Ru–S1	S5–Ru–S1 89.49(10)	92.1(1)	90.4(1)	97.1(1)
P1–Ru–S3	S6–Ru–S2 178.05(9)	176.8(1)	175.1(2)	175.2(1)
P1–Ru–P2	S5–Ru–S6 94.32(9)	94.6(1)	92.1(1)	93.9(1)

The Ru centers in all four complexes are pseudo-octahedrally coordinated by six S or four S and two P atoms. The thiolate S atoms occupy *trans* positions, while the thioether S atoms occupy *cis* positions. The DMSO ligands in **1** are coordinated via their S atoms. The Ru–S2 and Ru–S3 distances in **3b** · 0.5 MeOH (and the corresponding Ru–S2 and Ru–S2a distances in **3c**) are slightly shorter than the analogous distances in **3d** (236 vs. 239 pm). This result might be an indication of a correlation with the Ru–P distances, which are about 4 pm shorter in **3d** than in **3b** · 0.5 MeOH or **3c**. Although the cone angles[10] of PMe$_3$ (118°) and P*n*Pr$_3$ or P*n*Bu$_3$ (130°) differ markedly, their influence on the P–Ru–P angles of **3b** · 0.5 MeOH, **3c**, and **3d** is only slight. Thus, the three bis(alkylphosphane) complexes are structurally very similar. This may explain why the P*n*Pr$_3$ and P*n*Bu$_3$ complexes **3b** and **3c** are as inert towards substitution as the PMe$_3$ complex **3d**, and why only the [Ru(PPh$_3$)$_2$("S$_4$")] complex is substitution labile. The molecular structure of [Ru(PPh$_3$)$_2$("S$_4$")] is not yet known, but the structure of the related [Ru(PPh$_3$)$_2$("MeS$_4$")], in which "Me-S$_4$" denotes the "S$_4$" derivative bearing a methyl substituent on the C$_2$ bridge between the C$_6$H$_4$S$_2$ units, has been elucidated[11]. Here, the cone angle of PPh$_3$ (145°) leads to a significant increase of both the corresponding P–Ru–P angle [101.8(1)°] and the Ru–P bond lengths (237.3 pm).

Electrochemical Properties of [Ru(P*n*Bu$_3$)$_2$("S$_4$")] (3c) and [μ-S$_2${Ru(PCy$_3$)("S$_4$")}$_2$] (8b)

The good solubility of **3c** and **8b** allowed cyclic voltammograms (CV) to be recorded. Figure 4 shows the CVs of **3c** and **8b**. Selected electrochemical parameters and the assigned redox couples are listed in Table 2.

Figure 4. Cyclic voltammograms of a) **3c** and b) **8b** (v = 50 mV/s, CH_2Cl_2, *E* vs. NHE)

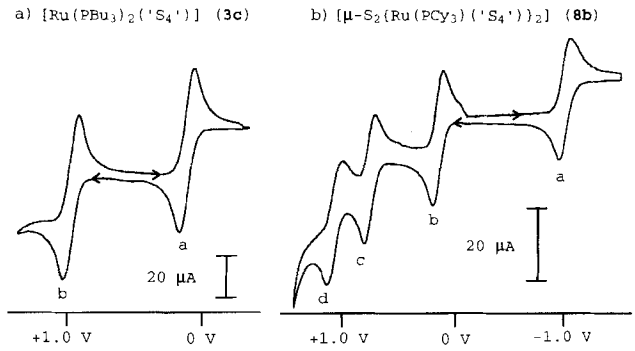


Table 2. Electrochemical parameters of **3c** and **8b** (potentials vs. NHE)

3c			**8b**		
redox couple	redox wave	*E*'[V][a]	redox couple	redox wave	*E*'[V]
---	---	---	$[X]^0/[X]^-$	a	−0.93
$[X]^0/[X]^+$	a	+0.05	$[X]^0/[X]^+$	b	+0.18
---	---	---	$[X]^+/[X]^{2+}$	c	+0.79
$[X]^+/[X]^{2+}$	b	+1.03	$[X]^{2+}/[X]^{3+}$	d	+1.11

[a] Half-wave potential.

The cyclic voltammograms of **3c** and **8b** exhibit two and four quasi-reversible redox waves, respectively. The two anodic redox waves of **3c** can be plausibly assigned to Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} redox couples. Analogously, the three anodic redox waves of **8b** can be assigned to Ru^{II}/Ru^{III}, Ru^{III}/Ru^{III}, and Ru^{III}/Ru^{IV} species. A Ru^{IV}/Ru^{IV} species appears to be inaccessible. This may be due to the strong electronic coupling between the two Ru centers in **8b**. This coupling is evident from the electronic spectrum of the complex (see above), and here from the redox potentials which increase with every oxidation. In contrast to **3c**, the

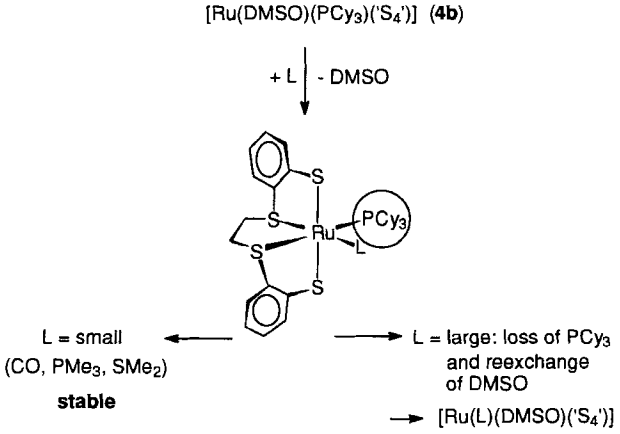
S_2 complex **8b** shows a cathodic wave. It can be assigned to a reduction of **8b** yielding a Ru^{II}/Ru^{I} species.

Discussion and Summary

New complexes with [Ru("S_4")] fragments have been synthesized via [Ru(DMSO)$_2$("S_4")] (**1**) from [Ru(Cl)$_2$-(DMSO)$_4$] and "S_4"-Na_2. [Ru(DMSO)$_2$("S_4")] (**1**) contains labile DMSO ligands which coordinate via their S atoms. The DMSO ligands can be exchanged for alkylphosphanes. Small phosphanes yield the bis(phosphane) derivatives [Ru(PR$_3$)$_2$("S_4")] (R = Et **3a**, *n*Pr **3b**, *n*Bu **3c**), while bulkier phosphanes such as P*i*Pr$_3$ and PCy$_3$ give the monophosphane derivatives [Ru(DMSO)(PR$_3$)("S_4")] (R = *i*Pr **4a**, Cy **4b**). Substitution of both DMSO ligands of [Ru(DMSO)$_2$("S_4")] (**1**) also occurs when **1** is treated with THT, thereby affording [Ru(THT)$_2$("S_4")] (**2**).

[Ru(DMSO)(PCy$_3$)("S_4")] (**4b**) proved to be particularly well-suited for further substitution reactions. The coligands PCy$_3$ and DMSO in **4b** are both labile, but which one is substituted depends critically on the reaction partner. The reaction of **4b** with P*n*Pr$_3$ or P*n*Bu$_3$ leads to an exchange of PCy$_3$ yielding the phosphane/DMSO complexes [Ru(DMSO)(P*n*R$_3$)("S_4")] (R = Pr **4c**, Bu **4d**), while sterically less demanding ligands such as PMe$_3$ and SMe$_2$ give [Ru(PMe$_3$)(PCy$_3$)("S_4")] (**6**) and [Ru(SMe$_2$)(PCy$_3$)("S_4")] (**7**). This substitution behavior of [Ru(DMSO)(PCy$_3$)("S_4")] (**4b**) can be explained by assuming that the primary step is invariably a substitution of the DMSO ligand, yielding a [Ru(L)(PCy$_3$)("S_4")] derivative according to Scheme 2.

Scheme 2. Reactions of [Ru(DMSO)(PCy$_3$)("S_4")] (**4b**)



If L is (relatively) large, such as P*n*Pr$_3$ or P*n*Bu$_3$, the resultant [Ru(L)(PCy$_3$)("S_4")] complexes become sterically overcrowded. The PCy$_3$ ligand, which is inherently labile due to its large cone angle, is further labilized and thus is displaced by the initially released DMSO. However, if L is small (PMe$_3$, CO, SMe$_2$), the resultant [Ru(L)(PCy$_3$)("S_4")] species become stable and can be isolated. This explanation is supported by the fact that the reaction of [Ru(PMe$_3$)(P-Cy$_3$)("S_4")] (**6**) with CO yields [Ru(CO)(PMe$_3$)("S_4")], showing that PCy$_3$ is more labile than PMe$_3$. Also consistent with this explanation is the fact that the DMSO/phosphane complexes [Ru(DMSO)(PR$_3$)("S_4")] (R = *i*Pr **4a**, Cy **4b**, *n*Bu **4d**) react with CO to give [Ru(CO)(PR$_3$)("S_4")] (R = *i*Pr **5a**, Cy **5b**, *n*Bu **5c**). The required reaction conditions, which are more drastic in the case of **4d**, indicate the influence of the phosphane size upon the DMSO labilization in [Ru(DMSO)(PR$_3$)("S_4")] complexes.

The bis(*n*-alkylphosphane) complexes [Ru(PR$_3$)$_2$("S_4")] (R = Et **3a**, *n*Pr **3b**, *n*Bu **3c**) proved to be as inert towards substitution as the previously reported [Ru(PMe$_3$)$_2$("S_4")] (**3d**). By comparison of the molecular structures it is clear that **3b**, **3c**, and **3d** differ only marginally in their structural features. A noticeable labilization of the phosphane ligands can only be expected in the case of ligands exhibiting significantly larger cone angles (and sizes) such as, e.g., PPh$_3$ or PCy$_3$.

All of the [Ru(L)(L')("S_4")] complexes described here exhibit much greater solubility than previously synthesized complexes containing the [Ru(PPh$_3$)("S_4")] subunit. For example, the [Ru(DMSO)(PR$_3$)("S_4")] (R = *i*Pr **4a**, Cy **4b**) complexes proved to be excellent starting materials for the synthesis of very soluble μ-S_2 complexes [μ-S_2{Ru(PR$_3$)("S_4")}$_2$] (R = *i*Pr **8a**, Cy **8b**). The spectroscopic properties of these complexes and four quasi-reversible redox waves in the cyclic voltammogram of **8b** indicate a strong electronic coupling of the Ru centers via the S_2 bridges. Experiments are presently being carried out with the aim of isolating the electrochemically observed redox species, and also to employ **4a** and **4b** for the synthesis of complexes with nitrogeneous ligands.

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Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded with the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated): Perkin-Elmer 983, 1620 FT IR and 16PC FT-IR. – NMR: Jeol FT-JNM-GX 270, EX 270 and Lambda LA 400. – ^1H and $^{13}C\{^1H\}$ NMR: The protio-solvent signal was used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. – $^{31}P\{^1H\}$ NMR: Spectra were recorded with H_3PO_4 as an external standard. – Elemental analyses: Carlo-Erba EA 1106 and 1108. – MS: Varian MAT 212. – UV/Vis: Shimadzu UV-3101 PC. – Cyclic voltammetry was performed with a PAR 264A potentiostat using a three electrode cell with glassy carbon ROTEL A working, Ag/AgCl reference and Pt counter electrodes. Solutions were 10^{-3} M in the substance under investigation. $TBAPF_6$ (10^{-1} M) was used as supporting electrolyte. Potentials were referred to NHE via Fc/Fc^+ as internal standard (E_{Fc/Fc^+} = +0.4 V vs. NHE[12]).

"S_4"-H_2[13], [Ru(Cl)$_2$(DMSO)$_4$][9], P*i*Pr$_3$[14], PCy$_3$[15], and [Ru(PMe$_3$)$_2$("S_4")] (**3d**)[5a] were prepared as described in the literature.

[Ru(DMSO)$_2$("S_4")] (**1**): [Ru(Cl)$_2$(DMSO)$_4$] (242 mg, 0.5 mmol) was added to a solution of NaOMe (200 mg, 3.7 mmol) and "S_4"-H_2 (155 mg, 0.5 mmol) in 15 ml of MeOH. After 5 min, a yellow solid started to precipitate from the orange solution. The

suspension was stirred for 3 d and then the resultant solid was separated, washed with 9 ml of MeOH and dried in vacuo. Yield: 245 mg **1** · 0.5 MeOH (84%). – $C_{18.5}H_{26}O_{2.5}RuS_6$ (581.86): calcd. C 38.19, H 4.50, S 33.06; found C 38.30, H 4.17, S 33.02. – IR (KBr): $\tilde{\nu}$ = 1020, 1076 cm^{-1} (SO). – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.65 (d, 2H, C_6H_4), 7.40 (d, 2H, C_6H_4), 7.10 (t, 2H, C_6H_4), 6.90 (t, 2H, C_6H_4), 3.35 (s, 3H, SCH_3), 3.00 (s, 3H, SCH_3), 2.90 (d, 2H, C_2H_4), 2.15 (d, 2H, C_2H_4). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 156.4, 131.9, 131.7, 130.8, 129.2, 122.7 [C(aryl)], 46.4, 45.3 (SCH_3), 40.5 (C_2H_4). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 566 $[Ru(DMSO)_2("S_4")]^+$.

[Ru(THT)$_2$("S$_4$")] (**2**): $[Ru(Cl)_2(DMSO)_4]$ (484 mg, 1.0 mmol) and 4 ml of THT were added to a solution of NaOMe (220 mg, 4.1 mmol) and "S_4"-H_2 (310 mg, 1.0 mmol) in 20 ml of MeOH. A yellow suspension resulted which was stirred for 2 h at 40°C and for 12 h at room temperature. The resultant yellow precipitate was separated, washed with 20 ml of MeOH and 10 ml of Et_2O, and dried in vacuo. Yield: 435 mg **2** · 0.25 Et_2O (72%). – $C_{23}H_{30.5}O_{0.25}RuS_6$ (604.46): calcd. C 45.70, H 5.09, S 31.83; found C 45.59, H 5.16, S 32.10. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.50 (d, 2H, C_6H_4), 7.40 (d, 2H, C_6H_4), 6.95 (t, 2H, C_6H_4), 6.85 (t, 2H, C_6H_4), 2.90 (m, 8H, THT), 2.70 (d, 2H, C_2H_4), 1.90 (m, 8H, THT), 1.75 (d, 2H, C_2H_4). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CH_2Cl_2): δ = 158.0, 133.5, 131.6, 130.6, 128.4, 121.6 [C(aryl)], 40.8 (C_2H_4), 36.9, 32.0, 31.4, 30.7 [C(THT)]. – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 586 $[Ru(THT)_2("S_4")]^+$.

[Ru(PEt$_3$)$_2$("S$_4$")] (**3a**): PEt_3 (0.35 ml, 2.5 mmol) was added to a suspension of NaOMe (342 mg, 6.3 mmol), "S_4"-H_2 (152 mg, 0.5 mmol), and $[Ru(Cl)_2(DMSO)_4]$ (242 mg, 0.5 mmol) in 20 ml of MeOH. The resultant yellow solution was heated under reflux for 2 h. After cooling to room temperature, yellow microcrystals precipitated which were separated after 12 h, washed with 15 ml of MeOH, and dried in vacuo. Yield: 235 mg (73%). – $C_{26}H_{42}P_2RuS_4$ (645.88): calcd. C 48.35, H 6.55, S 19.86; found C 48.27, H 6.59, S 19.84. – IR (KBr): $\tilde{\nu}$ = 1085 cm^{-1} δ(PCH). – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (d, 2H, C_6H_4), 7.45 (d, 2H, C_6H_4), 6.95 (t, 2H, C_6H_4), 6.80 (t, 2H, C_6H_4), 2.85 (d, 2H, C_2H_4), 1.90 (m, 14H, C_2H_4, PCH_2), 1.05 (m, 18H, CH_3). – $^{13}C\{^1H\}$ NMR (100.40 MHz, $CDCl_3$): δ = 160.3 (t), 131.8, 131.3, 130.5, 127.9, 120.9 [C(aryl)], 39.9 (t, J_{PC} = 5.0 Hz) (C_2H_4), 19.4 (m), 8.3 (t, J_{PC} = 2.48 Hz) $[P(C_2H_5)_3]$. – $^{31}P\{^1H\}$ NMR (109.38 MHz, $CDCl_3$): δ = +18.5 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 646 $[Ru(PEt_3)_2("S_4")]^+$.

[Ru(PR$_3$)$_2$("S$_4$")] (R = *n*Pr **3b**, *n*Bu **3c**). – *General Procedure:* $[Ru(Cl)_2(DMSO)_4]$, PR_3, NaOMe, and "S_4"-H_2 were combined in MeOH. The resultant red solution was heated under reflux for 2 h, cooled to room temperature and reduced in volume to 5 ml. A yellow solid precipitated which was separated, washed with 15 ml of MeOH, and dried in vacuo.

[Ru(PnPr$_3$)$_2$("S$_4$")] (**3b**): 140 mg (2.6 mmol) of NaOMe; 153 mg (0.5 mmol) of "S_4-H_2"; 30 ml of MeOH; 240 mg (0.5 mmol) of $[RuCl_2(DMSO)_4]$; 0.7 ml (2.5 mmol) of $PnPr_3$. Yield: 155 mg (42%). – $C_{32}H_{54}P_2RuS_4$ (730.04): calcd. C 52.65, H 7.46, S 17.57; found C 52.43, H 7.65, S 17.31. – IR (KBr): $\tilde{\nu}$ = 1078 cm^{-1} δ(PCH). – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (d, 2H, C_6H_4), 7.40 (d, 2H, C_6H_4), 6.95 (t, 2H, C_6H_4), 6.80 (t, 2H, C_6H_4), 2.80 (d, 2H, C_2H_4), 1.90 (d, 2H, C_2H_4), 1.80 (m, 12H, CH_2), 1.45 (m, 12H, CH_2), 0.90 (t, 18H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, $CDCl_3$): δ = 161.1 (d, J_{PC} = 2.7 Hz), 132.5, 132.0, 131.0, 128.5, 121.5 [C(aryl)], 40.6 (d, J_{PC} = 5.4 Hz) (C_2H_4), 30.3 (t, J_{PC} = 10.7 Hz), 18.1, 16.6 (t, J_{PC} = 6.7 Hz) $[P(C_3H_7)_3]$. – $^{31}P\{^1H\}$ NMR (109.38 MHz, $CDCl_3$): δ = +12.5 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 730 $[Ru(PnPr_3)_2("S_4")]^+$.

[Ru(PnBu$_3$)$_2$("S$_4$")] (**3c**): 150 mg (2.8 mmol) of NaOMe; 155 mg (0.5 mmol) of "S_4"-H_2; 20 ml of MeOH; 254 mg (0.5 mmol) of $[RuCl_2(DMSO)_4]$; 0.7 ml (2.5 mmol) of $PnBu_3$. Yield: 295 mg (72%). – $C_{38}H_{66}P_2RuS_4$ (814.20): calcd. C 56.06, H 8.17, S 15.75; found C 56.28, H 8.22, S 15.70. – IR (KBr): $\tilde{\nu}$ = 1089 cm^{-1} δ(PCH). – ^1H NMR (269.6 MHz, $CDCl_3$): δ = 7.55 (d, 2H, C_6H_4), 7.40 (d, 2H, C_6H_4), 6.95 (t, 2H, C_6H_4), 6.80 (t, 2H, C_6H_4), 2.80 (d, 2H, C_2H_4), 1.90 (d, 2H, C_2H_4), 1.85 (m, 12H, CH_2), 1.45 (m, 24H, CH_2), 0.85 (m, 18H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, $CDCl_3$): δ = 161.7, 132.4, 131.8, 130.4, 128.0, 120.8 [C(aryl)], 40.3 (C_2H_4), 27.5, 26.1, 24.8, 14.0 $[P(C_4H_9)_3]$. – $^{31}P\{^1H\}$ NMR (109.38 MHz, $CDCl_3$): δ = +13.2 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 814 $[Ru(PnBu_3)_2("S_4")]^+$.

[Ru(DMSO)(PR$_3$)("S$_4$")] (R = *i*Pr **4a**, Cy **4b**). – *General Procedure:* $[Ru(Cl)_2(DMSO)_4]$, PR_3, NaOMe, and "S_4"-H_2 were combined in MeOH yielding a yellow suspension. This suspension was then heated under reflux for 12 h, whereupon a blue color developed and a yellow solid precipitated. After cooling to room temperature, the solid was separated, washed with 30 ml of MeOH and 30 ml of Et_2O, and dried in vacuo.

[Ru(DMSO)(PiPr$_3$)("S$_4$")] (**4a**): 146 mg (2.7 mmol) of NaOMe; 310 mg (1 mmol) of "S_4"-H_2; 20 ml of MeOH; 484 mg (1 mmol) of $[Ru(Cl)_2(DMSO)_4]$; 1 ml (5.1 mmol) of $PiPr_3$. Yield: 550 mg (85%). – $C_{25}H_{39}OPRuS_5$ (631.96): calcd. C 46.34, H 6.07, S 24.74; found C 46.03, H 6.16, S 24.47. – IR (KBr): $\tilde{\nu}$ = 1087 cm^{-1} (SO). – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (d, 1H, C_6H_4), 7.45 (d, 2H, C_6H_4), 7.33 (d, 1H, C_6H_4), 7.00 (q, 2H, C_6H_4), 7.85 (m, 2H, C_6H_4), 3.30 (s, 3H, SCH_3), 2.72 (s, 3H, SCH_3), 2.72 (m, 5H, C_2H_4, PCH), 1.90 (d, 2H, C_2H_4), 1.40 (m, 9H, CH_3), 1.20 (m, 9H, CH_3). – $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ = 159.1, 132.8, 131.8 (d), 131.6, 131.2 (d), 131.0, 130.3, 129.0, 128.8, 121.9, 121.8 [C(aryl)], 50.5, 45.3 (SCH_3), 42.3 (d), 38.9 (C_2H_4), 27.8 (d, J_{PC} = 19.1 Hz), 20.4, 20.0 (PC_3H_7). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +35.7 (s).

[Ru(DMSO)(PCy$_3$)("S$_4$")] (**4b**): 460 mg (8.5 mmol) of NaOMe; 637 mg (2.05 mmol) of "S_4"-H_2; 35 ml of MeOH; 1.0 g (2.05 mmol) of $[RuCl_2(DMSO)_4]$; 2.0 g (7.1 mmol) of PCy_3. Yield: 1.385 g (88%) yellow powder. – $C_{34}H_{51}OPRuS_5$ (768.12): calcd. C 53.16, H 6.69, S 20.87; found C 53.40, H 6.55, S 20.46. – IR (KBr): $\tilde{\nu}$ = 1088 cm^{-1} (SO). – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.60 (m, 1H, C_6H_4), 7.45 (m, 2H, C_6H_4), 7.37 (m, 1H, C_6H_4), 7.00 (m, 2H, C_6H_4), 6.85 (m, 2H, C_6H_4), 3.30 (s, 3H, SCH_3), 2.80 (m, 1H, C_2H_4), 2.75 (m, 1H, C_2H_4), 2.70 (s, 3H, SCH_3), 2.45–0.85 [m, 35H, C_2H_4, $P(C_6H_{11})_3$]. – $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ = 162.4 (d), 160.8, 133.9, 132.2, 131.8, 131.5, 131.4, 130.7, 129.0, 128.9, 122.1, 121.8 [C(aryl)], 50.1, 45.1 (SCH_3), 42.4 (d), 39.2 (C_2H_4), 38.7 (br.), 30.6 (br.), 29.1 (d, J_{PC} = 10.0 Hz), 29.1 (d, J_{PC} = 9.1 Hz), 27.7 ($P(C_6H_{11})_3$). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +26.2 (s). – FD MS (70 eV, THF, ^{102}Ru); *m/z*: 662 $[Ru(PCy_3)("S_2")_2]^+$.

[Ru(DMSO)(PCy$_3$)("S$_4$")] (**4b**) *from Isolated [Ru(DMSO)$_2$("S$_4$")]* (**1**) *and PCy$_3$:* A brown suspension of (**1**) (218 mg, 0.39 mmol) and PCy_3 (380 mg, 1.3 mmol) in 15 ml of THF was heated under reflux for 12 h. After cooling to room temperature, the resultant green solution was filtered and reduced in volume to 5 ml. After the addition of 50 ml of MeOH, the solution was cooled to −20°C. Precipitated yellow crystals were separated after 7 d, washed with 10 ml of Et_2O and dried in vacuo. Yield: 120 mg (41%). The yellow crystals were identified by elemental analysis and spectroscopic methods.

[Ru(DMSO)(PR$_3$)("S$_4$")] (R = *n*Pr **4c**, *n*Bu **4d**) – *General Procedure:* An equimolar amount of PR_3 was added to a yellow-green suspension of [Ru(DMSO)(PCy_3)("S_4")] (**4b**) in 10 ml of THF at −78 °C. The resultant yellow suspension was stirred at −78 °C for 30 min, warmed to room temperature, and then stirred for a further 2 h. A brown-yellow solution resulted, which was concentrated to dryness. The remaining solid was redissolved in 10 ml of Et_2O. The resultant solution was filtered and cooled to −30 °C. Precipitated yellow crystals were separated after 2 d, washed with 10 ml of Et_2O, and dried in vacuo.

[Ru(DMSO)(PnPr$_3$)("S$_4$")] (**4c**): 353 mg (0.46 mmol) of **4b**; 0.092 ml (0.46 mmol) of P*n*Pr$_3$. Yield: 185 mg (62%). – $C_{25}H_{39}OPRuS_5$ (647.96): calcd. C 46.34, H 6.07, S 24.74; found C 46.60, H 6.55, S 24.49. – IR (KBr): $\tilde{\nu}$ = 1087 cm^{-1} (SO). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.60–7.30 (m, 4H, C_6H_4), 7.05–6.75 (m, 4H, C_6H_4), 3.25 (s, 3H, SCH_3), 2.90 (m, 2H, C_2H_4), 2.75 (s, 3H, SCH_3), 2.00–1.30 [m, 14H, C_2H_4, $P(C_2H_4)_3$], 0.95 (t, 9H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 159.9 (d), 158.6, 134.3, 132.7, 132.1, 131.8, 131.0, 130.3, 130.2, 128.8, 128.7, 121.9, 121.8 [C(aryl)], 50.5, 45.1 (SCH_3), 42.0 (d), 39.2 (C_2H_4), 28.4 (d, $^1J_{PC}$ = 25 Hz), 17.6 (d, J_{PC} = 4 Hz), 16.0 (d, J_{PC} = 13.5 Hz) (PC_3H_7). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +17.0 (s). – FD MS (70 eV, THF, ^{102}Ru); *m/z*: 648 [Ru(DMSO)(P*n*Pr$_3$)("S_4")]$^+$.

[Ru(DMSO)(PnBu$_3$)("S$_4$")] (**4d**): 401 mg (0.52 mmol) of **4b**; 0.13 ml (0.52 mmol) of P*n*Bu$_3$. Yield: 190 mg (54%). – $C_{28}H_{45}OPRuS_5$ (690.04): calcd. C 48.74, H 6.57, S 23.23; found C 48.86, H 6.26, S 23.17. – IR (KBr): $\tilde{\nu}$ = 1088 cm^{-1} (SO). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (m, 1H, C_6H_4), 7.45 (m, 2H, C_6H_4), 7.35 (d, 1H, C_6H_4), 6.95 (m, 2H, C_6H_4), 6.85 (m, 2H, C_6H_4), 3.25 (s, 3H, SCH_3), 2.90 (m, 2H, C_2H_4), 2.75 (s, 3H, SCH_3), 2.00–1.20 (m, 20H, C_2H_4, CH_2), 1.85 (t, 9H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 160.0, 158.7, 132.8, 132.1, 131.8, 131.1, 130.4, 130.3, 128.8, 128.7, 121.8, 121.7 [C(aryl)], 50.5, 45.1 (SCH_3), 41.0, 39.2 (C_2H_4), 26.0 (t), 25.7, 24.7 (d), 13.9 ($P(C_4H_9)_3$). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +17.1 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 690 [Ru(DMSO)(P*n*BU$_3$)("S_4")]$^+$.

[Ru(CO)(PiPr$_3$)("S$_4$")] (**5a**): CO gas was bubbled through a green-yellow suspension of [Ru(DMSO)(P*i*Pr$_3$)("S_4")] (**4a**) (307 mg, 0.47 mmol) in 30 ml of THF for 45 min. A yellow-brown solution resulted to which 75 ml of *n*-hexane was added. The slightly cloudy solution was filtered, and the volume of the filtrate was reduced to ca. 3 ml. A yellow solid precipitated which was separated, washed with 4 ml of *n*-hexane, and dried in vacuo. Yield: 196 mg (70%). – $C_{24}H_{33}OPRuS_4$ (597.83): calcd. C 48.22, H 5.56, S 21.45; found C 47.89, H 5.70, S 21.19. – IR (KBr): $\tilde{\nu}$ = 1955 cm^{-1} (CO). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.50–7.40 (m, 3H, C_6H_4), 7.35 (m, 1H, C_6H_4), 7.10–6.80 (m, 4H, C_6H_4), 3.15 (m, 1H, C_2H_4), 2.95 (m, 1H, C_2H_4), 2.55 (m, 3H, CH), 2.15 (m, 1H, C_2H_4), 1.95 (m, 1H, C_2H_4), 1.35 (m, 9H, CH_3), 1.25 (m, 9H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, $CDCl_3$): δ = 201.1 (d) (CO), 158.7, 158.2 (d), 132.3, 132.1, 131.6, 131.5, 131.2, 129.9, 129.6, 129.2, 122.9, 122.6 [C(aryl)], 41.3 (d), 41.1 (C_2H_4), 27.0 (d, J_{PC} = 22.0 Hz), 20.22, 20.05 [$P(C_3H_7)$]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +51.0 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 598 [Ru(CO)(P*i*Pr$_3$)("S_4")]$^+$.

[Ru(CO)(PCy$_3$)("S$_4$")] (**5b**): CO gas was bubbled through a green-yellow suspension of [Ru(DMSO)(PCy_3)("S_4")] (**4b**) (373 mg, 0.49 mmol) in 25 ml of THF for 30 min. The resultant yellow-brown solution was concentrated to dryness, and the remaining residue was redissolved in 3 ml of THF. After the addition of 10 ml of MeOH, the solution was cooled to −78 °C. Yellow microcrystals precipitated which were separated after 1 d, washed with 15 ml of MeOH, and dried in vacuo. Yield: 355 mg **5b** · MeOH (96%). – $C_{34}H_{49}O_2PRuS_4$ (750.07): calcd. C 54.45, H 6.58, S 17.10; found C 54.53, H 7.09, S 16.76. – IR (KBr): $\tilde{\nu}$ = 1954 cm^{-1} (CO). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (m, 2H, C_6H_4), 7.43 (m, 1H, C_6H_4), 7.30 (m, 3H, C_6H_4), 7.00 (m, 2H, C_6H_4), 6.85 (m, 2H, C_6H_4), 3.10 (m, 1H, C_2H_4), 2.93 (m, 1H, C_2H_4), 2.35–0.95 (m, 35H, C_2H_4, $P(C_6H_{11})_3$). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 159.1, 158.6 (d, J_{PC} = 5.3 Hz), 132.3, 132.2, 131.7, 131.6, 131.4, 130.1, 129.5, 129.2, 122.8, 122.6 [C(aryl)], 41.6 (d, J_{PC} = 9.5 Hz), 41.0 (C_2H_4), 36.6 (d, J_{PC} = 20.1 Hz), 30.0, 28.4 (d, J_{PC} = 9.4 Hz), 28.3 (d, J_{PC} = 9.6 Hz), 27.1 [$P(C_6H_{11})_3$]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +39.2 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 718 [Ru(CO)(PCy_3)("S_4")]$^+$.

[Ru(CO)(PnBu$_3$)("S$_4$")] (**5c**): A yellow solution of [Ru(DMSO)(P*n*Bu$_3$)("S_4")] (**4d**) (180 mg, 0.26 mmol) in 15 ml of THF was treated with CO gas (30 bar) in an autoclave for 24 h. The resultant bright-yellow solution was then concentrated to dryness. Yield: 163 mg (98%). – $C_{27}H_{39}OPRuS_4$ (639.89): calcd. C 50.68, H 6.14, S 20.04; found C 50.43, H 6.06, S 20.66. – IR (KBr): $\tilde{\nu}$ = 1960 cm^{-1} (CO). – ^{1}H NMR (269.6 MHz, $CDCl_3$): δ = 7.75–7.35 (m, 4H, C_6H_4), 7.80–7.10 (m, 4H, C_6H_4), 3.10 (m, 2H, C_2H_4), 2.15 (m, 2H, C_2H_4), 2.10–1.70 (m, 8H, PCH_2), 1.60–1.35 [m, 12H, (CH_2)], 0.95 (t, 9H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, $CDCl_3$): δ = 199.2 (d, J_{PC} = 16.1 Hz) (CO), 158.6, 157.4 (d, J_{PC} = 5.4 Hz), 131.8, 131.0, 130.6, 130.5, 129.1, 128.8, 128.7, 122.2, 121.8 [C(aryl)], 40.9, 40.4 (d, J_{PC} = 10.7 Hz) (C_2H_4), 25.8 (d, J_{PC} = 28.3 Hz), 25.1 (d, J_{PC} = 2.7 Hz), 24.1 (d, J_{PC} = 12.1 Hz), 13.6 [$P(C_4H_9)_3$]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, $CDCl_3$): δ = +21.5 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 640 [Ru(CO)(P*n*Bu$_3$)("S_4")]$^+$.

[Ru(PMe$_3$)(PCy$_3$)("S$_4$")] (**6**): At −78 °C, PMe_3 (0.04 ml, 0.39 mmol) was added to a green-yellow suspension of **4b** (298 mg, 0.39 mmol) in 10 ml of THF. The resultant suspension was warmed to room temperature yielding a red-brown solution in the course of 2 h. The solution was concentrated to dryness and the remaining residue was stirred with 20 ml of Et_2O for 2 h. The resultant yellow precipitate was separated, washed with 15 ml of Et_2O, and dried in vacuo. Yield: 210 mg (69%). – $C_{35}H_{54}P_2RuS_4$ (766.10): calcd. C 54.87, H 7.10, S 16.74; found C 54.59, H 7.40, S 16.62. – IR (KBr): $\tilde{\nu}$ = 955 cm^{-1} δ(PCH). – ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55–7.45 (m, 4H, C_6H_4), 7.00–6.70 (m, 4H, C_6H_4), 2.85 (m, 1H, C_2H_4), 2.65 (m, 1H, C_2H_4), 2.15–0.80 [m, 35H, C_2H_4, $P(C_6H_{11})_3$], 1.35 [d, 9H, $P(CH_3)_3$]. – $^{13}C\{^1H\}$ (67.7 MHz, CD_2Cl_2): δ = 161.3 (d, J_{PC} = 5.4 Hz), 160.7 (d, J_{PC} = 6.7 Hz), 133.3, 132.3, 131.7 (d, J_{PC} = 2.7 Hz), 130.6 (d, J_{PC} = 2.7 Hz), 130.3, 130.1, 128.1, 128.0, 121.3, 120.8 [C(aryl)], 40.5 (d, J_{PC} = 10.7 Hz), 39.7 (d, J_{PC} = 13.4 Hz) (C_2H_4), 39.5 (br), 30.2 (m), 28.4 (d, J_{PC} = 9.4 Hz), 26.8, 27.5–26.4 (m) [$P(C_4H_9)_3$], 19.7 (d, J_{PC} = 28.2 Hz) (PMe_3). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = −8.25 (d) (PMe_3), +27.25 (PCy_3). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 766 [Ru(P-Me_3)(PCy_3)("S_4")]$^+$.

[Ru(SMe$_2$)(PCy$_3$)("S$_4$")] (**7**): SMe_2 (1 ml, 13.4 mmol) was added to a suspension of [Ru(DMSO)(PCy_3)("S_4")] (**4b**) (379 mg, 0.5 mmol) in 10 ml of THF and the mixture was stirred for 12 h at room temperature. The resultant dark-yellow solution was reduced in volume to ca. 5 ml and combined with 20 ml of MeOH. A yellow solid precipitated which was separated, washed with 10 ml of MeOH and 10 ml of Et_2O, and dried in vacuo. Yield: 365 mg **7** · 0.5 THF (90%). – $C_{36}H_{55}O_{0.5}PRuS_5$ (812.18): calcd. C 54.86, H 7.03, S 20.34; found C 55.15, H 7.09, S 20.28. – ^{1}H NMR (269.6

MHz, CD_2Cl_2): δ = 7.45 (m, 3H, C_6H_4), 7.35 (m, 1H, C_6H_4), 6.95 (m, 2H, C_6H_4), 6.80 (m, 2H, C_6H_4), 2.70 (m, 1H, C_2H_4), 2.60 (m, 1H, C_2H_4), 2.10 (s, 6H, SCH_3), 2.05–0.85 [m, 35H, C_2H_4, $P(C_6H_{11})_3$]. – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 161.3 (d), 159.2, 134.6, 132.6, 131.4, 131.1 (d), 130.7, 130.0, 128.4, 128.3, 121.4, 121.1 [C(aryl)], 42.8, 37.9 (C_2H_4), 37.3 (d, J_{PC} = 16.1 Hz), 29.7 (br), 28.3 (d, J_{PC} = 9.4 Hz), 27.0 [$P(C_6H_{11})_3$], 22.2 (SCH_3). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +26.5 (s). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 662 $[Ru(PCy_3)("S_2")_2]^+$.

[μ-S$_2${Ru(PiPr$_3$)("S$_4$")}$_2$] (**8a**): S_8 (109 mg, 0.42 mmol) was added to a green-yellow suspension of [Ru(DMSO)(P*i*Pr$_3$)("S$_4$")] (**4a**) (276 mg, 0.43 mmol) in 10 ml of THF and the mixture was stirred at room temperature. The color of the suspension turned blue and grey microcrystals precipitated which were separated after 1 d, washed with 20 ml of THF and 5 ml of Et_2O, dried in vacuo for 5 min, and redissolved in 20 ml of hot toluene. The resultant blue solution was filtered and stored at 5°C. Dark-blue crystals precipitated which were separated after 1 d, washed with 15 ml of Et_2O, and dried in vacuo. Yield: 100 mg **8a** · 0.5 Et_2O (38%). – $C_{48}H_{71}O_{0.5}P_2Ru_2S_{10}$ (1240.84): calcd. C 46.46, H 5.77, S 25.84; found C 46.52, H 5.42, S 25.56. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55–7.30 (m, 8H, C_6H_4), 7.10–6.90 (m, 6H, C_6H_4), 6.80 (m, 2H, C_6H_4), 2.95 (m, 2H, C_6H_4), 2.65 (m, 2H, C_6H_4), 2.25 (m, 6H, CH), 2.05 (m, 2H, C_2H_4), 1.85 (m, 2H, C_2H_4), 1.20–0.95 (m, 36H, CH_3). – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 160.36 (d), 159.87, 132.83, 131.71, 131.45, 130.34, 130.12, 128.71, 128.63, 123.29, 121.77 [C(aryl)], 44.75 (d), 40.99 (C_2H_4), 27.13 (d, J_{PC} = 19.8 Hz), 19.84 (d, J_{PC} = 23.1 Hz), 19.83 (d, J_{PC} = 24.1 Hz) [$P(C_3H_7)$]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +40.5 (s). – UV (CH_2Cl_2, [nm]): 1150 (ε = 9028 l mol^{-1}), 720 (ε = 9714 l mol^{-1}), 594 (ε = 5754 l mol^{-1}), 448 (ε = 2853 l mol^{-1}). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 1203 $[\mu\text{-}S_2\{Ru(PiPr_3)("S_4")\}_2 - H]^+$.

[μ-S$_2${Ru(PCy$_3$)("S$_4$")}$_2$] (**8b**): At room temperature, addition of S_8 (77 mg, 0.30 mmol) to a stirred suspension of [Ru(DMSO)(P-Cy_3)("S_4")] (**4b**) (940 mg, 1.22 mmol) in 20 ml of THF, led to an immediate color change from yellow to blue. Over a period of 2 h, complete dissolution of the complex occurred, affording a blue solution which was filtered and concentrated to dryness. The dark-blue residue was redissolved in 8 ml of CH_2Cl_2, the resultant solution was filtered and cooled to −78°C. Dark-blue crystals precipitated which were separated, washed with 5 ml of cold CH_2Cl_2 and 15 ml of Et_2O, and dried in vacuo. Yield: 687 mg **8b** · 0.5 CH_2Cl_2 (79%). – $C_{64.5}H_{91}ClP_2Ru_2S_{10}$ (1486.63): calcd. C 52.11, H 6.17, S 21.57; found C 52.00, H 6.38, S 21.80. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.55 (m, 4H, C_6H_4), 7.45 (m, 2H, C_6H_4), 7.35 (m, 2H, C_6H_4), 7.10–6.85 (m, 6H, C_6H_4), 6.80 (m, 2H, C_6H_4), 2.95 (m, 2H, C_2H_4), 2.70 (m, 2H, C_2H_4), 2.10–0.95 [m, 70H, C_2H_4, $P(C_6H_{11})$]. – $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 160.5, 133.4, 131.7, 131.3, 130.4, 130.2, 130.1, 128.8, 128.7, 122.6, 121.8 [C(aryl)], 45.0, 41.3 (C_2H_4), 37.6 (d, J_{PC} = 16.2 Hz), 29.8, 28.2 (d, J_{PC} = 6.5 Hz), 27.8 (d, J_{PC} = 6.5 Hz), 27.0 [$P(C_6H_{11})_3$]. – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = +31.0 (s). – UV (CH_2Cl_2, [nm]): 1150 (ε = 12863 l mol^{-1}), 736 (ε = 10675 l mol^{-1}), 580 (ε = 6863 l mol^{-1}). – FD MS (70 eV, CH_2Cl_2, ^{102}Ru); *m/z*: 1444 $[\mu\text{-}S_2\{Ru(PCy_3)("S_4")\}_2]^+$.

X-ray Structure Analyses of [Ru(DMSO)$_2$("S$_4$")] (**1**), *[Ru(PnPr$_3$)$_2$("S$_4$")]* · *0.5 MeOH* (**3b** · 0.5 MeOH), *[Ru(PnBu$_3$)$_2$("S$_4$")]* (**3c**) *and [Ru(PMe$_3$)$_2$("S$_4$")]* (**3d**): Bright-green cuboids of **1** were obtained when a saturated solution in

Table 3. Selected crystallographic data of **1**, **3b** · 0.5 CH_3OH, **3c**, and **3d**

Compound	**1**	**3b** · 0.5 CH_3OH	**3c**	**3d**
formula	$C_{18}H_{24}O_2RuS_6$	$C_{32.5}H_{56}O_{0.5}P_2RuS_4$	$C_{38}H_{66}P_2RuS_4$	$C_{20}H_{32}P_2RuS_4$
M_r [g/mol]	565.80	746.0	814.2	563.6
crystal size [mm]	0.4 × 0.2 × 0.2	0.9 × 0.8 × 0.8	0.5 × 0.4 × 0.2	0.5 × 0.1 × 0.1
F(000)	1152	3144	1728	5184
space group	$P2_1/n$	*C*2/*c*	*C*2/*c*	$R\bar{3}$
cryst. syst.	monoclinic	monoclinic	monoclinic	trigonal
a [pm]	1112.8(4)	1494.4(15)	2182.7(12)	2463.5(11)
b [pm]	1703.0(9)	1767.8(29)	1643.0(7)	2463.5(11)
c [pm]	1147.1(5)	2889.4(31)	1190.3(6)	2145.1(12)
β [°]	94.13(3)	98.86(9)	105.99(4)	--------
V [nm^3]	2.168(2)	7.543(16)	4.104(3)	11.274(12)
Z	4	8	4	18
$D_{calcd.}$ [g/cm^3]	1.733	1.31	1.32	1.49
μ [mm^{-1}]	1.313	0.744	0.689	1.030
diffractometer	Siemens P4	Siemens P4	Siemens P4	Nicolet R3m/V
radiation [pm]		Mo-Kα (λ = 71.073)		
temperature [K]	200	200	200	293
scan technique	ω-scan	ω-scan	ω-scan	ω-scan
2Θ range [°]	4–51	3–54	3–54	4–54
scan speed [°/min]	3.00–30.00	3.00–29.30	3.00–29.30	3.00–15.00
meas. reflections	5276	12865	5631	8705
indep. reflections	3902	8263	4511	4983
$R_{int.}$ [%]	5.97	13.07	5.18	2.11
obsd. reflections	1715	6207	2227	2077
σ criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 5\sigma(F)$
R; R_w [%]	5.11; 15.80[a]	4.80; 4.31	4.72; 4.01	6.40; 4.00
refined parameters	340	356	204	293

[a] wR_2 (refinement on F^2 using SHELXL-93[17]).

CH_2Cl_2 was layered with MeOH/Et_2O. Yellow prisms of **3b** · 0.5 MeOH formed when a THF solution of **3b** was layered with MeOH and cooled from 20 °C to −20 °C. Yellow prisms of **3c** were obtained by cooling a saturated MeOH solution from 20 °C to −20 °C. Yellow needles of **3d** were obtained by cooling a saturated CH_2Cl_2 solution from 20 °C to −20 °C. The single crystals were sealed under N_2 in glass capillaries. Data were corrected for Lorentz and polarization effects while an absorption correction has not been applied. The structures were solved by direct methods (SHELXTL-PLUS)[16]. Full-matrix least-squares refinement was carried out on F^2 values for **1** (SHELXL-93)[17] and on *F* values for **3b**, **3c**, and **3d**, respectively[16]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in the difference Fourier synthesis and either restricted during refinement (**3b**, **3c**) or isotropically refined (**1**). In the case of [Ru(PMe_3)$_2$("S_4")] (**3d**), the hydrogen atoms of the phenyl groups were placed at calculated positions and refined as rigid groups; the hydrogen atoms of methyl and methylene groups were placed in ideal tetrahedral positions and allowed to rotate around their central carbon atom during refinement. Selected crystallographic data are summarized in Table 3[18].

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[18] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-406168 [Ru(DMSO)$_2$("S_4"), CSD-405993 [Ru(P*n*Pr$_3$)$_2$("S_4")] · 0.5 MeOH, CSD-405994 [Ru(P*n*Bu$_3$)$_2$("S_4")], CSD-405995 [Ru(PMe_3)$_2$("S_4")], the names of the authors, and the journal citation.

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